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Transformation of Polycyclic Aromatic Hydrocarbons during Sampling

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Individual PAH are shown to undergo chemical transformation when exposed to gases such as NO_2, O_3 and SO_3. The possibility of artifact formation during sampling in stacks and in ambient air is discussed. PAH on soot, formed in a smoke gas generator, and exposed to NO_x and SO_x in a thermostated oven were degraded as a result of the sampling technique. Addition of NO_2 (1 ppm) or gaseous HNO_3 (120 ppb) during ambient air sampling caused degradation of individual PAH on particles and formation of the corresponding mononitro-PAH. Addition of 200 ppb O_3 or 100 ppb gaseous HNO_2 had no detectable effect. Thus, artifact formation can occur as a result of the presence of NO_2, HNO_3, or SO_x both in stack gas sampling and in sampling of PAH on particles in ambient air.

Introduction

During the last few years, the interest in sampling and analysis of polycyclic aromatic hydrocarbons (PAH) from different sources and in ambient air has increased rapidly. Together with the chemical analysis, the mutagenic activity is often studied by using the Ames' Salmonella/liver microsome assay. During the same period of time several papers have been published concerning reactions between individual PAH and gases such as NO, NO_2, O_3 and SO_3. Benzo(a)pyrene (BaP) and perylene adsorbed on glass fiber filters will thus form nitro derivatives by exposure to NO_2 and traces of nitric acid (*1*).

In experiments where pyrene and BaP were exposed to NO, NO_2, SO_2 or SO_3, degradation was obtained with NO_2 and SO_3 (*2*). It is thus evident that some PAH can react with NO_2 and SO_3 while NO and SO_2 seem to be without effect. The mononitro derivatives formed have proved to be direct mutagenes (*1,3*). Further experiments with BaP exposed to ozone demonstrated the production of directly mutagenic compounds, one of which was later reported to be benzo(a)pyrene-4,5-oxide (*3*).

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NO_x and SO_x are present in the stack gas at combustion of fossil fuels. During sampling of PAH in stack gas, the NO_x and SO_x will pass through the collected materials during several hours, and consequently there is a risk that transformation reactions will take place and lead to an underestimate of the PAH content. As some of the transformation products are direct mutagens, the formation of these sampling artifacts would give rise to an erroneous conception of the mutagenic effect of the stack gas.

In ambient air, the concentrations of NO_x and SO_x are usually much lower, but the primarily emitted gases will be transformed in the atmosphere to more oxidized and acidic forms. Due to this and to the long sampling time required, artifact formation can still occur and lead to incorrect results.

The reactivity has turned out to be dependent on the kind of carrier on which the individual compound is adsorbed (*2,4,5*). In most of the experiments published previously, solutions of pure compounds have been sprayed on filters with or without particles. In this procedure either the whole amount of the compound or an unknown part of it will be in contact with the filter surface (run-off effect). Both in emission samples and ambient air samples the main part of the PAH collected on filters is adsorbed

on particles, and consequently only a minor part will be in direct contact with the filter surface. The method with "spiking" filters is therefore inappropriate for studying sampling artifacts. A more relevant result could be obtained if different filters were used simultaneously in collecting particles from ambient air. This was done by Lee et al. (*5*), who found that filters of glass fibers and microglass fibers with Teflon binder both gave a lower yield of PAH compared with the Teflon membrane filter when airborne particulates were collected. In an additional experiment, the filter effect in diesel exhaust sampling was studied. In contrast to the other experiments, no artifact formation was obtained. The effect of filter types in sampling of diesel engine particulate exhaust has been investigated further by Clark et al. (*6*). No major differences in relative concentrations were observed, and no differences in mutagenicity of the samples could be detected. Since the sampling time is short and the concentrations of NO_2 are rather low (ca. 500 ppb) this result is not surprising.

The PAH emitted from incomplete combustion of organic material is formed together with soot, and at least some of the PAH will then be attached to soot particles. Recently, a study was published in which soot and PAH were generated by combustion of ethene, transferred to a reaction chamber, and exposed to NO_x, about 10 ppm, for 5-51 days (*7*). Under these conditions the half-life of BaP was 7 days. Exposure to air containing 5 ppm SO_2 for 99 days did not affect the recoveries of PAH. Unfortunately, these experiments were carried out in dry air and thus the conditions are not comparable with those of stack gas. NO and NO_2 are acid anhydrides and form HNO_2 and HNO_3 in the presence of water vapor, which seems to play an important role in the degradation of PAH (*1,8*).

The physical and chemical properties of soot particles depend partly on the fuel. Soot particles formed by combustion of volatile hydrocarbons in a smoke gas generator may thus differ from those formed by combustion of other fuels. Yet, soot/PAH generated in this way can be considered relevant in artifact formation studies, particularly as the smoke also contains moisture.

In order to find out if artifact formation can take place during stack gas sampling, the degradation of PAH exposed to NO_x and SO_x was studied in a set of experiments (*9*). Soot and PAH were generated in a smoke gas generator, attached to a thermostated oven, by combustion of propane in the presence of a limited amount of air. The gases were added just before the oven. All experiments were carried out with rather high NO_2 concentrations (100-200 ppm) compared to what is usually found in stack gases, but this was to some extent compensated for with short exposure times. The sampling method tested includes separation of particles at stack gas temperature, collecting of condensate and adsorption of not condensed compounds on Amberlite XAD-2. The results indicate that degradation or transformation of reactive PAHs takes place under certain circumstances and that these reactions may occur during the sampling. The concentration of BaP was reduced up to 50% as a result of the sampling technique, while the concentration of benzo(a)anthracene (BaA) was reduced up to 90%. In this case, however, the reduction can partly be ascribed to reactions occurring during the exposure of the gases in the oven. Simultaneous exposure to SO_3 increased the degradation of BaP, BaA and pyrene, thus indicating that SO_3 is a reactive species in the degradation of individual PAH. No degradation occurred in the condensate or on the XAD-2. The results obtained in this study emphasize the necessity of further studies of artifact formation during sampling of PAH from stack gases.

Another investigation was carried out in 1980 to study the possible occurrence of degradation of PAH and the formation of mutagenic compounds through reactions with NO_2 and O_3 during sampling of particulate PAH from the atmosphere (*10*). This investigation was followed by a second study in 1981 with exposure to NO_2, HNO_2 and HNO_3 (*11*). The main purpose this time was to investigate the importance of the active agent and to identify at least some of the reaction products.

Experimental

To avoid false carrier effect and other disturbances, we found it necessary to carry out the studies in the way the high-volume sampling of atmospheric PAH is usually made. The experiments were therefore carried out outdoors with existing particulate PAH. Two high-volume samplers were run simultaneously (24-hr sampling). One of them was equipped with different dosage systems which increased the concentration of the actual gas.

In the first series of experiments sampling with NO_2 addition (ca. 1 ppm) was carried out for five 24-hr periods and with O_3 addition (ca. 200 ppb) for three 24-hr periods. The experiments were carried out at an air quality monitoring station in central Göteborg, about 20 m above street level. The concentrations of SO_2, NO, NO_2, O_3 and nonmethane hydrocarbons (NMHC), as well as some meteorological parameters, were measured continuously.

After sampling, the filters were Soxhlet-extracted for 24 hr with acetone. 2-Methylanthracene and 1-methylpyrene were added as internal standards

and the extract was diluted with water and shaken with cyclohexane. The cyclohexane phase was then subjected to a liquid-liquid extraction with dimethylformamide (DMF)/water, (9:1) and a subsequent back-extraction of PAH from the DMF phase by addition of water and cyclohexane. After concentration, the cyclohexane phase was analyzed on a Carlo Erba gas chromatograph with a glass capillary column (SE-54). In addition to chemical analysis of the PAH content, tests for mutagenic activity in the Ames Salmonella/microsome test and ability to displace 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) from the rat liver receptor protein were made (*12*).

In 1981 eight experiments with each gas (NO_2, HNO_2 and HNO_3) were carried out (*11*). As in the first experiments, the NO_2 was delivered from a gas bottle. Gaseous HNO_2 was prepared by adding, slowly and under intense mixing, a dilute solution of $NaNO_2$ to a dilute H_2SO_4 solution. Purified air was allowed to flow into the reaction vessel, and the outlet air stream was mixed with ambient air just before the filter in the sampler. The concentration of gaseous HNO_2 in the total airflow passing through the filter was estimated to 100 ± 20 ppb. In the HNO_3 experiments, 20 mL of concentrated HNO_3 was added to a 100 mL Pyrex glass cup placed in a circular acrylic frame, which was attached to the funnel of the high-volume sampler. The vapor pressure of HNO_3 was then sufficiently high to obtain a concentration of HNO_3 gas in the ambient airflow of 120 15 ppb. After sampling, the filters were extracted separately, but the extracts were combined in order to facilitate an identification of the reaction products. Of each of the combined extracts, 12% was submitted to the Ames Salmonella/microsome test and 6% was used in an analysis of PAH as described above. The remaining 82% was fractionated by HPLC (Spherisorb 5 ODS) to give one PAH fraction and one mononitro-PAH fraction (*13*). The individual mononitro-PAHs were then identified by GC^2-MS selected ion monitoring technique using ions obtained from mass spectra of reference substances.

Results and Discussion

The amount and number of PAHs detected varied from day to day. In the first series of experiments, eight PAH were found in detectable amounts in all samples. The differences in PAH concentration between exposed and nonexposed filters were calculated. We found that exposure to 200 ppb O_3 had very little effect. Significant degradation occurred in one of the experiments only and in the biological tests there was no detectable influence. On the other hand, exposure to 1 ppm NO_2 caused degradation of pyrene, BaA and BaP, while phenantrene and benzofluoranthenes seem to be resistant to chemical reaction. The degradation increased in the presence of acid on the particles. The increase in mutagenic effect was, on the average, 4-fold, while the affinity to the receptor protein was unchanged. Thus, it is evident that exposure to NO_2 during sampling can lead to losses of some PAH. Since the losses are not related to any physical properties of the compounds, e.g., vapor pressure, and are followed by a significant increase in the Salmonella mutagenicity, the most probable explanation is chemical transformation.

As mentioned above, the filter extracts were combined in the second series of experiments. Furthermore, another clean-up procedure was used. Because of this, the concentrations of individual PAH obtained may not be correct. The concentrations of the eight PAH studied were in the range 0.3/-3 ng/m^3.

Instead of comparing the concentrations of individual PAH from nonexposed and exposed filters directly, we compared the PAH profiles, calculated relative to benzo(e)pyrene (BeP), which was found stable throughout the experiments. We found that exposure to 100 ppb HNO_2 did not cause any degradation of PAH. The only nitro-PAH found, most probably 9-nitroanthracene, was found in all the other samples as well. Exposure to 1 ppm NO_2 gave rise to degradation of BaA (20%), BaP (35%) and perylene (35%) and a corresponding formation of 10-nitro-BaA and 6-nitro-BaP. Some 3-nitropyrene was found as well, but no nitroperylene could be detected.

The most pronounced effect was found in the experiment with HNO_3. For BaP, the loss was about 95% while the concentrations of BaA and perylene decreased by 55% and benzo(g,h,i)perylene by 20%. In the mononitro fraction, four of the corresponding reaction products—nitropyrene (two isomers), 10-nitro-BaA and 6-nitro-BaP—were found.

The chemical changes were in accordance with the results of the Ames Salmonella/microsome test (*14*). No effect of exposure to HNO_2 could be detected, while both NO_2 and HNO_3 gave rise to an increased number of revertants/m^3. The increase was greater in the test without addition of rat liver microsomes which indicates an increase of directly mutagenic compounds, e.g., mononitro PAH.

Exposure to NO_2 and HNO_3 during sampling evidently causes degradation of the individual PAH and a corresponding formation of mononitro PAH. HNO_3 has a greater nitrating effect than NO_2. This theory is further supported by the results of the Ames test, the effect of acid, mentioned above, and a good agreement with the Nielsen reactivity scale (*8*), which is based on results attained in solutions

containing H^+, NO_3^-, HNO_2 and minute amounts of N_2O_4.

Conclusions

Exposure to NO_2 and HNO_3 during sampling will cause degradation of individual PAH. If we assume that the degradation is due to nitration and has a first-order dependence on the concentration of NO_2, the expected degradation at different levels of NO_2 in the atmosphere can be calculated from our data. Within the range of NO_2 concentrations normally formed in urban air (<0.3 ppm), the degradation of BaP during sampling could amount to 20-40%. At higher temperatures (>0°C), it may be even more.

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